Definitive Quality Control of Titania Coatings with the Agilent 7020 ZetaProbe

Application Note

Abstract

Commercial titania particles are nearly always coated with a substance such as silica or alumina to prevent breakdown under sunlight. The Agilent 7020 ZetaProbe is ideal for monitoring the type and the integrity of this surface coating, and for this reason, it is used in the quality control (QC) labs of titania manufacturers and their customers to detect any batch-to-batch variability.

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The importance of coatings for titania

Titania (TiO_2) is a white pigment and an important industrial material, widely used in the paint, ink, paper, synthetic fiber, and even cosmetic industries. It is used as a coating, a reflecting agent, or as a scatterer/absorber of light. In its pure form, titania suffers from the drawback that it is *photoactive*, so when it is acted on by light, it can release an electron from its surface and that electron may cause chemical damage to the surrounding material over time. Thus, for example, a paint that is made using uncoated titania particles will crack and deteriorate under prolonged exposure to sunlight. For this reason, the titania particles are usually covered with a thin layer of some other oxide, like silica, alumina, or zirconia, or some combination of these materials.

Titration using the ZetaProbe reveals surface coating

The ZetaProbe has proved to be a vital QC tool for controlling the surface coating in the titania manufacturing process. The QC is usually done by carrying out a pH titration on a sample from the process stream to determine the curve of zeta against pH.

Two sample ZetaProbe titration curves are shown in Figure 1. The first is for an uncoated titania, while the second is for a silica-coated titania. Clearly, the curves are strongly influenced by the type of coating. In practice, attention is usually focused on the *isoelectric point* (IEP), which is the pH at which zeta is zero. For the uncoated titania particles, the IEP is 6.2, but for the silica-coated particles it is below pH 2, which is typical of a pure silica particle. For alumina-coated particles on the other hand, the IEP is up around 9.

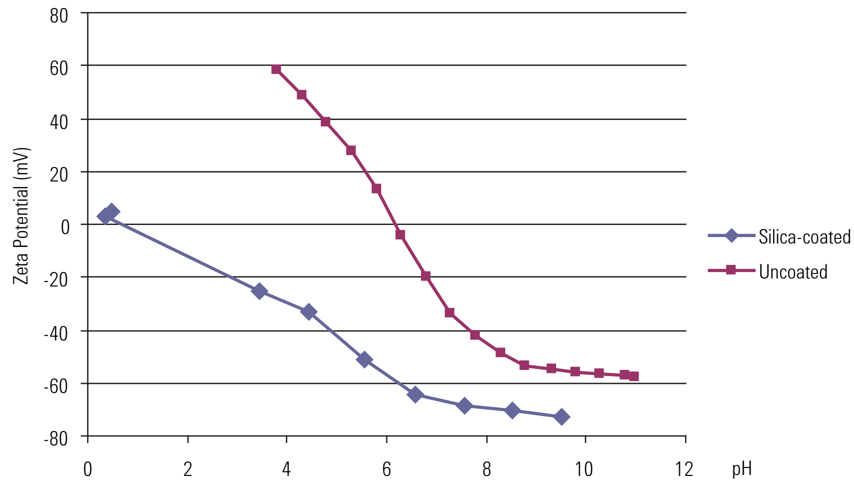

Figure 1. ZetaProbe titration curve for uncoated titania shows an IEP of 6.2, while that of silica-coated titania shows an IEP of less than 2, allowing one to easily distinguish the two surfaces.

Thus, the IEP provides a clear indication of the type and the integrity of the coating on the titania particles. If the coverage is patchy or if it is too thin, the IEP will be shifted. For each batch of titania, the IEP is measured and compared to the standard value for that coating grade.

The ZetaProbe is ideal for this application, because it has been designed for easy and accurate IEP determination. Its computer-controlled burettes and rapid measurement processes allow the IEP to be determined to better than 0.1 pH units in under half an hour. This is critical for the QC labs where throughput is vital.

The various optical devices for measuring zeta are inherently slower and far less accurate than the ZetaProbe because they require sample dilution, which is both time-consuming and which introduces errors due to changes in the supernatant or contamination of particle surface by trace surface-active materials. The ZetaProbe does not require sample dilution because it uses our patented electroacoustic technique, which can be applied to concentrated suspensions.

Electroacoustic measurement provides insight into the coating process

The titration curve for the silica-coated titania in Figure 1 has the same form as for a pure silica particle. Clearly in this case the coating is thick enough to completely mask the underlying titania, but how thick does the coating have to be for complete coverage, and what happens with thinner layers?

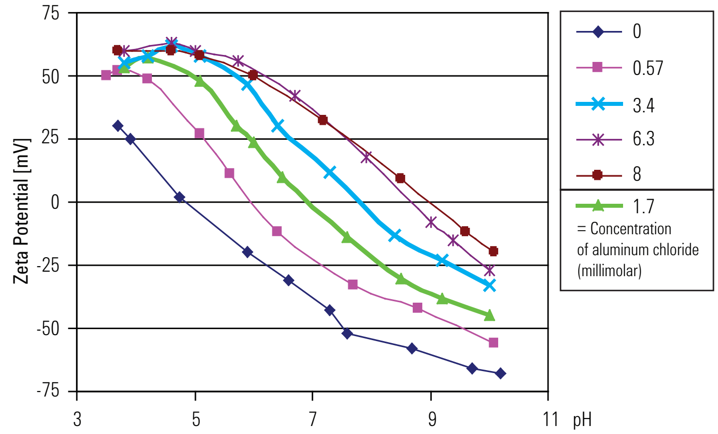

Figure 2. Electrostatic potential near a negatively charged spherical particle

An answer to the second question is provided by the data in the Figure 2, which shows the electroacoustic zeta curves for titania particles during an alumina deposition process. In this experiment, progressively larger quantities of aluminum (as aluminum chloride or nitrate) were added to the titania colloidal solution. After each addition (at low pH), the pH was raised, causing the Al^{3+} ion to hydrolyze and become adsorbed on the particle surface as the oxide or hydroxide. The initial titania was uncoated and had its natural IEP at about pH 5. When coating was complete, the IEP had shifted up to pH 9.1, a value characteristic of the alumina-covered surface.

Djedjev et al recently carried out a detailed study of silica coating on titania using a combination of electroacoustic, dielectric response, and transmission electron microscopy (TEM) measurements of the coating layer [1]. They found that the IEP drops to the limiting silica value when the coating is around one nm thick. Further increases in the coating layer do not alter the titration curve any more. From the dielectric measurements, they determined that the dielectric constant of the coating is around 20, higher than the value for pure silica. The authors take this to be an indication of hydrolysis within the silica layer.

Conclusion

The Agilent 7020 ZetaProbe is an excellent tool for quality control of surface coating in the titania manufacturing process. The isoelectric point – the pH at which the zeta potential is zero – differs depending on the type and integrity of the surface coating. The ZetaProbe enables very easy, rapid, and accurate determination of a plot of zeta potential versus pH, so it is an ideal instrument to assess the quality of the coating process. The ZetaProbe does not require sample dilution, so it saves time and avoids the errors that are inherent in optical measurement of zeta potential.

Reference

1. Djerdjev, A. M.; Beattie, J. K.; and O'Brien, R.W. (2005) "Coating of Silica on Titania Pigment Particles Examined by Electroacoustics and Dielectric Response." *Chemistry of Materials* **17 (15)** 3844-9.

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